

Viscosity Measurement and Correlation of the Squalane + CO₂ Mixture

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We report experimental results for the viscosity of the squalane + CO₂ mixtures. The viscosities were measured by using a rolling ball viscometer. The experimental temperatures were 293.15, 313.15, 333.15 and 353.15K, and pressures were 10, 15 and 20MPa. The mole fraction of CO₂ in the mixtures were 0.0, 0.095, 0.201, 0.362, and 0.417. The composition of the mixture was determined by weighing. The experimental uncertainties in temperature, pressure, and composition were estimated to be within $\pm 4\text{mK}$, $\pm 0.2\text{MPa}$, and $\pm 0.1\text{mole\%}$, respectively. The accuracy of the reported viscosity values was estimated to be $\pm 3.0\%$. Viscosity of mixtures reduces with the increase in CO₂ mole fraction. The experimental values were compared with the Grunberg-Nissan and the McAllister equations.

KEY WORDS: Grunberg-Nissan equation; McAllister equation; rolling ball; squalane; CO₂; viscosity.

1. INTRODUCTION

Natural refrigerants such as CO₂ draw much attention as replacing hydrochlorofluorocarbons (HCFCs) and/or hydrofluorocarbons (HFCs). The CO₂ has low ozone depletion potential and global warming potential compared to the HCFCs and/or HFCs. Furthermore, it is nontoxic and incombustible. When it is used as the refrigerant, the refrigeration system should be operated at higher pressure compared to the HCFCs and/or HFCs systems. However, as it has high ability

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on thermal properties, the system will be scaled down.

In refrigeration systems, the mixtures of a lubricating oil and refrigerant circulate in the system. So thermal properties of those mixtures over a wide range of composition, temperature and pressure are indispensable to optimum design of the refrigeration system. Additionally, the correlation and the prediction are very important because the required data do not often exist.

Squalane($C_{30}H_{62}$) can be a model substance for the lubricating oil because of its characteristic thermodynamic properties. The purpose of this study is to measure the viscosity of squalane + CO_2 mixture were measured at temperature range from 293.15 to 353.15K and pressure range from 10 to 20MPa and to correlate the data with Grunberg-Nissan and McAllister equations.

2. EXPERIMENTAL

The viscosity was measured by using a rolling ball viscometer. The viscometer used in this study is illustrated in Fig.1. The glass tube was approximately 10cm in length with an internal diameter of 7.09mm and a diameter of the stainless steel ball was 7.00mm. The upper part of the glass tube is open in order to make equal pressure of inside and outside of the glass tube. Pressure was regulated with moving a piston at a lower position of the viscometer with the use of pressure medium (silicon oil). The viscosity, η , was calculated from the fall time of the ball, t , by the following equation:

$$\eta = K(\rho_s - \rho)t \quad (1)$$

where K is the viscometer constant, and ρ_s and ρ are densities of the stainless steel ball and sample fluid, respectively. Since the viscometer constant was dependence of temperature, it was determined at each temperature. The viscometer constant at 293.15 and 313.15K was determined by using the standard liquids for calibrating of viscometer, that is, JS10, JS20, and JS50 calibrated by NRLM(Japan). The viscometer constant at 333.15 and 353.15K was determined by using ethylene glycol [1] because the standard liquids for calibration only assure of the viscosity and density values at 293.15, 303.15, and 313.15K. The density of a sample mixture was obtained by using a piezometer. The temperature of the thermostat was measured with a quartz thermometer, which was calibrated against a Leed-Northrup platinum resistance thermometer. The pressure was measured with a bourdon tube pressure gage, which was calibrated against a dead-weight gauge periodically. The composition of the mixture was determined by weighing. The experimental uncertainties in temperature, pressure, and composition were estimated within $\pm 4\text{mK}$, $\pm 0.2\text{MPa}$, $\pm 0.1\text{mole\%}$, respectively. The accuracy of the reported viscosity data was estimated to be $\pm 3.0\%$.

The squalane which had stated purity of 98.0mol% and CO_2 which had stated purity of 99.9mol% were purchased from Wako Pure Chemical Industries,Ltd. and Nippon Sanso Co., Ltd.(Japan), respectively. These substances were used without further purifications.

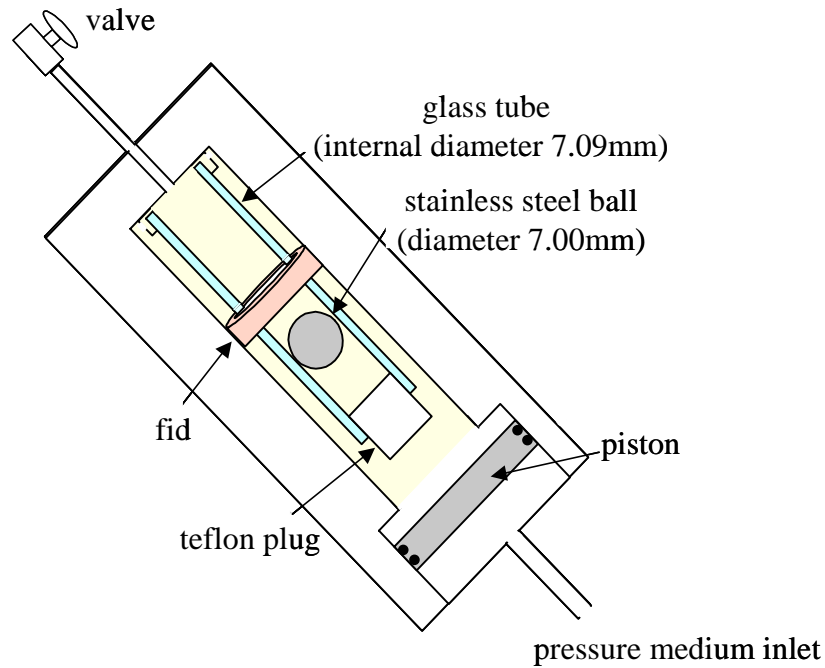


Fig.1 Rolling ball viscometer

3. RESULTS

The experimental viscosity data of the squalane + CO₂ mixture are given in Table 1 together with values for the density under the same conditions, which are interpolated from the experimental density values. The densities have an estimated accuracy of $\pm 0.2\%$. No literature viscosity values have been found for the mixtures studied here. For comparison purpose, the present viscosity data for the squalane at high pressure are shown in Table 2 together with our previously reported values which were obtained from a falling body viscometer [2]. The agreement between both data are satisfactory by considering the mutual experimental errors.

4. CORRELATION WITH THE GRUNBERG - NISSAN EQUATION

The viscosity of mixtures are often calculated from the viscosities of the pure components consisting of the mixtures. The Grunberg-Nissan equation is one of the most widely used viscosity correlation of liquid mixtures [3]. This simple empirical equation is written as,

$$\ln \eta = x_1 \ln \eta_1 + x_2 \ln \eta_2 + x_1 x_2 G \quad (2)$$

where η is the viscosity of mixture and η_i is the viscosity of pure component i at measurement condition. x_i is mole fraction of component i . G is the interaction parameter. Fig.2

Table 1 Viscosity for the Squalane + CO₂ Mixtures

T	x_1^*	P	ρ	η	T	x_1^*	P	ρ	η
[K]	[-]	[MPa]	[kg · m ⁻³]	[mPa · s]	[K]	[-]	[MPa]	[kg · m ⁻³]	[mPa · s]
293.15	0.000	10.0	812	44.3	333.15	0.000	10.0	792	9.37
		15.0	815	49.8			15.0	795	10.7
		20.0	817	55.6			20.0	798	11.5
	0.095	10.0	814	33.8		0.095	10.0	792	8.50
		15.0	817	38.4			15.0	795	9.24
		20.0	820	42.3			20.0	798	10.1
	0.201	10.0	817	29.1		0.201	10.0	793	7.38
		15.0	820	31.8			15.0	796	7.8
		20.0	822	35.9			20.0	799	8.85
	0.280	10.0	819	19.7		0.280	10.0	794	5.95
		15.0	821	22.5			15.0	797	6.44
		20.0	824	24.9			20.0	800	7.13
	0.362	10.0	821	17.0		0.362	10.0	795	5.50
		15.0	824	20.1			15.0	798	5.83
		20.0	826	22.2			20.0	801	6.44
	0.417	10.0	822	13.3		0.417	10.0	795	4.59
		15.0	825	14.9			15.0	798	4.92
		20.0	828	16.3			20.0	801	5.23
313.15	0.000	10.0	803	18.4	353.15	0.000	10.0	783	5.49
		15.0	806	20.7			15.0	786	5.98
		20.0	808	23.1			20.0	789	6.72
	0.095	10.0	803	16.0		0.095	10.0	782	5.01
		15.0	806	17.9			15.0	784	5.61
		20.0	809	19.2			20.0	784	5.95
	0.201	10.0	805	13.4		0.201	10.0	782	4.45
		15.0	808	15.3			15.0	784	4.77
		20.0	811	16.8			20.0	786	5.48
	0.280	10.0	806	10.5		0.280	10.0	782	3.78
		15.0	809	11.8			15.0	784	4.15
		20.0	812	12.5			20.0	787	4.56
	0.362	10.0	808	9.04		0.362	10.0	782	3.40
		15.0	810	10.1			15.0	784	3.73
		20.0	813	10.9			20.0	788	4.06
	0.417	10.0	808	7.35		0.417	10.0	782	3.03
		15.0	811	7.87			15.0	785	3.23
		20.0	814	8.41			20.0	789	3.42

* mole fraction of CO₂

Table2 Comparison of present viscosity data with previous ones.

T [K]	P [MPa]	present [mPa · s]	previous [mPa · s]*	Dev [%]**
293.15	10	44.3	43.6	1.6
	20	55.6	54.0	3.0
313.15	10	18.4	18.3	0.5
	20	23.1	22.7	1.8
333.15	10	9.37	9.43	-0.6
	20	11.5	11.0	4.5

*Ref. [2]

**Dev = $(\eta_{\text{present}} - \eta_{\text{previous}}) / \eta_{\text{previous}} \times 100$

shows interaction parameter G at 10MPa. When G was calculated by using of the experimental data, literature values were applied to the viscosity of pure CO_2 () [4]. It was found that G has dependence of mole fraction, temperature, and pressure. G increases linearly with the CO_2 mole fraction. But we could not express G as a function of temperature and pressure. So, the experimental data were correlated with the G expressed by linear function of the CO_2 mole fraction at each pressure and temperature. The equation of G and correlated results are shown in Table 3. Fig.3 shows the comparison of the experimental results at 10MPa and correlation with the Grunberg-Nissan equation. Fig.4 shows the deviation plot for the correlation with the Grunberg-Nissan equation. The Grunberg-Nissan equation correlated the experimental data with an AAD of 3.2% and maximum deviation of 10.0%.

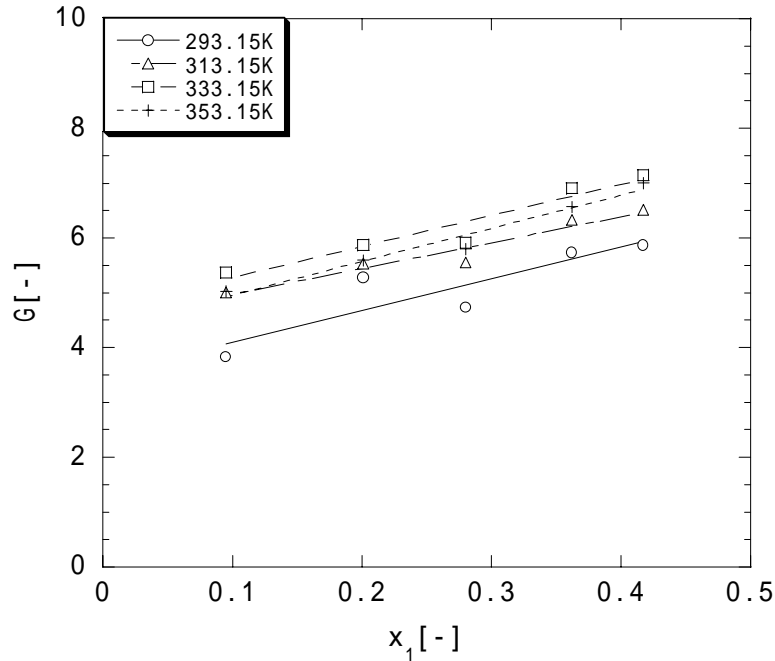


Fig.2 Dependence of G on mole fraction and temperature for squalane + CO_2 mixture (at 10MPa)

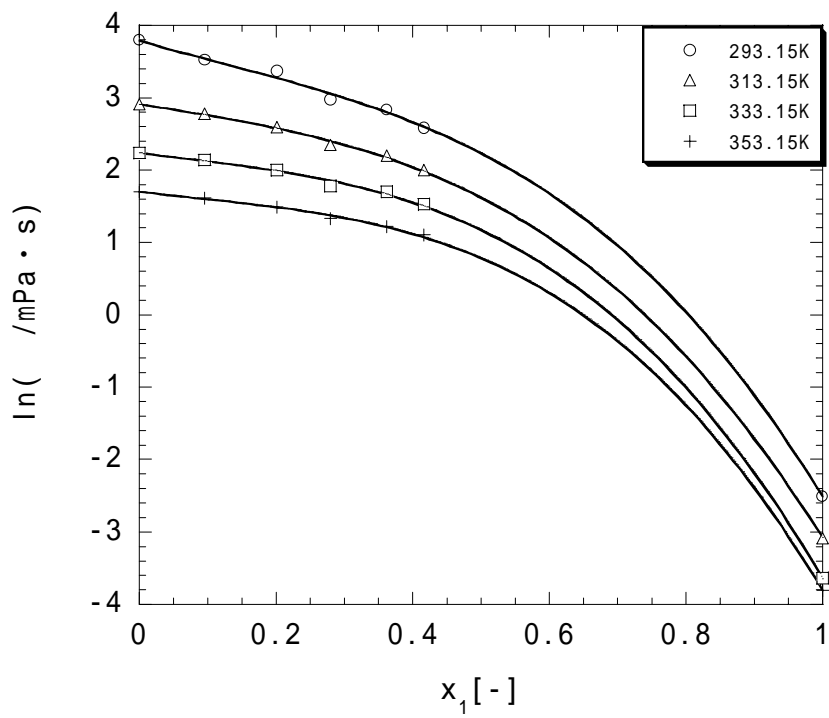


Fig.3 Comparison of the viscosity data of squalane + CO₂ mixture with correlation from the Grunberg-Nissan equation (at 10MPa) .

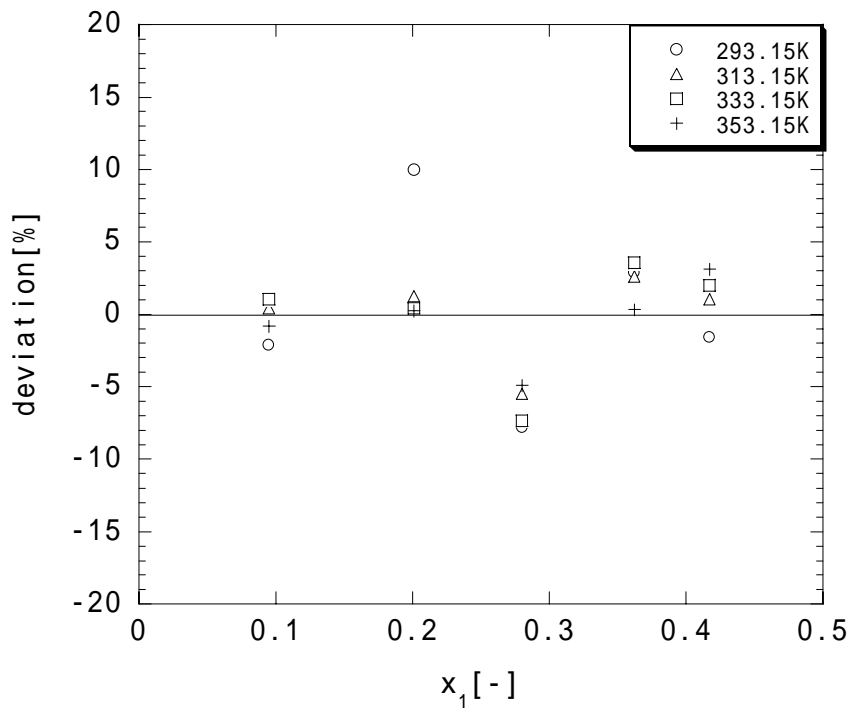


Fig.4 Deviation of viscosity of squalane + CO₂ mixtures between the experimental data and those calculated from the Grunberg-Nissan equation (at 10MPa).

Table 3 Parameters of the Grunberg -Nissan equation

T[K]	P[MPa]	G[-]	AAD*[%]	Max Dev. **[%]
293.15	10	$3.520+5.786x_I$	4.9	10.0
	15	$3.580+6.044x_I$	5.0	-7.2
	20	$3.473+5.979x_I$	5.7	8.5
313.15	10	$4.509+4.712x_I$	2.2	-5.5
	15	$4.337+3.781x_I$	2.7	-4.5
	20	$3.881+4.420x_I$	4.0	-5.2
333.15	10	$4.710+5.662x_I$	2.9	-7.4
	15	$3.677+5.837x_I$	2.0	-5.1
	20	$3.870+4.667x_I$	2.4	-4.9
353.15	10	$4.359+6.060x_I$	1.9	-4.9
	15	$4.357+4.628x_I$	2.8	-4.6
	20	$3.699+5.094x_I$	2.2	3.8

* Average absolute deviation = $(\eta_{\text{exp}} - \eta_{\text{calc}}) / \eta_{\text{calc}} \times 100$

** Max deviation = $(\eta_{\text{exp}} - \eta_{\text{calc}}) / \eta_{\text{calc}} \times 100$

5. CORRELATION WITH THE McALLISTER EQUATION

The McAllister equation is based on Eyring's absolute rate model for viscosity [5]. For the four-body McAllister model of the binary mixture, this semi-theoretical equation is written as,

$$\begin{aligned}
 \ln v = & x_1^4 \ln v_1 + 4x_1^3 x_2 \ln v_{1112} + 6x_1^2 x_2^2 \ln v_{1122} + 4x_1 x_2^3 \ln v_{2221} + x_2^4 \ln v_2 \\
 & - \ln \left[x_1 + x_2 \frac{M_2}{M_1} \right] + 4x_1^3 x_2 \ln \left[\frac{3 + M_2 / M_1}{4} \right] + 6x_1^2 x_2^2 \ln \left[\frac{1 + M_2 / M_1}{2} \right] \\
 & + 4x_1 x_2^3 \ln \left[\frac{1 + 3M_2 / M_1}{4} \right] + x_2^4 \ln \left[\frac{M_2}{M_1} \right]
 \end{aligned} \quad (3)$$

where v is the kinematic viscosity of mixture and v_i is the kinematic viscosity of pure component at measurement condition. x is the mole fraction and M is the molecular mass. v_{1112} , v_{1122} and v_{2221} are adjustable parameters and regressed by using experimental data with least-squares method at each temperature and pressure. The subscript 1 represents CO_2 and subscript 2 represents squalane. Since the molecular size ration of the squalane and CO_2 could be greater than 1.5, the four-body McAllister model should be applicable to the present system. The regressed values of the parameters of the McAllister equation are listed in Table 4. The comparison of the experimental results and the correlation with the McAllister equation is shown in Fig.5 and the deviations plot in Fig.6. This equation correlated the experimental data with an AAD of 2.9% and maximum deviation of 8.7%.

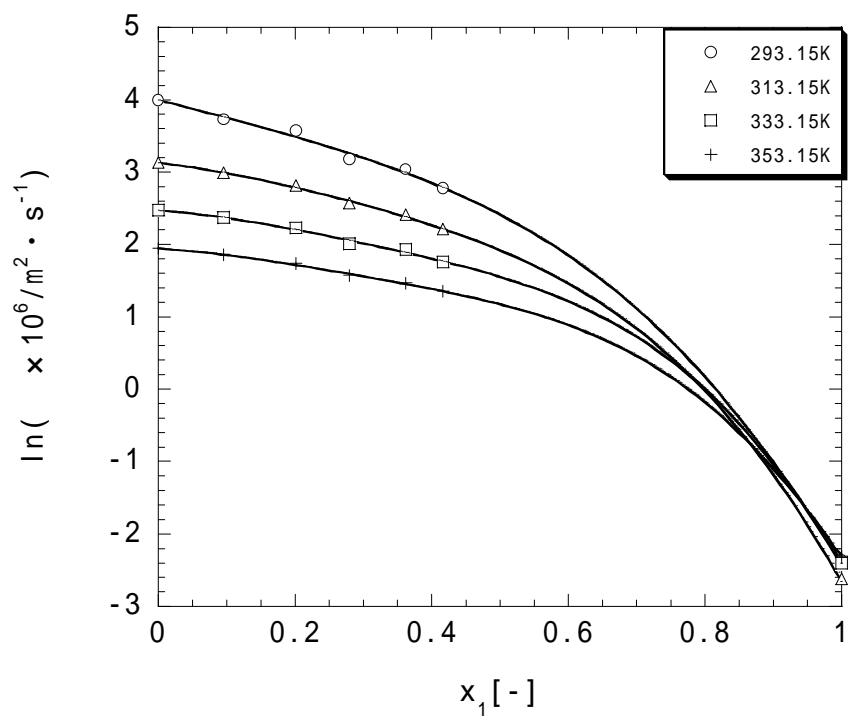


Fig.5 Comparison of the experimental kinematic viscosity data with ones correlated from the McAllister equation for squalane + CO₂ mixture (at 10MPa).

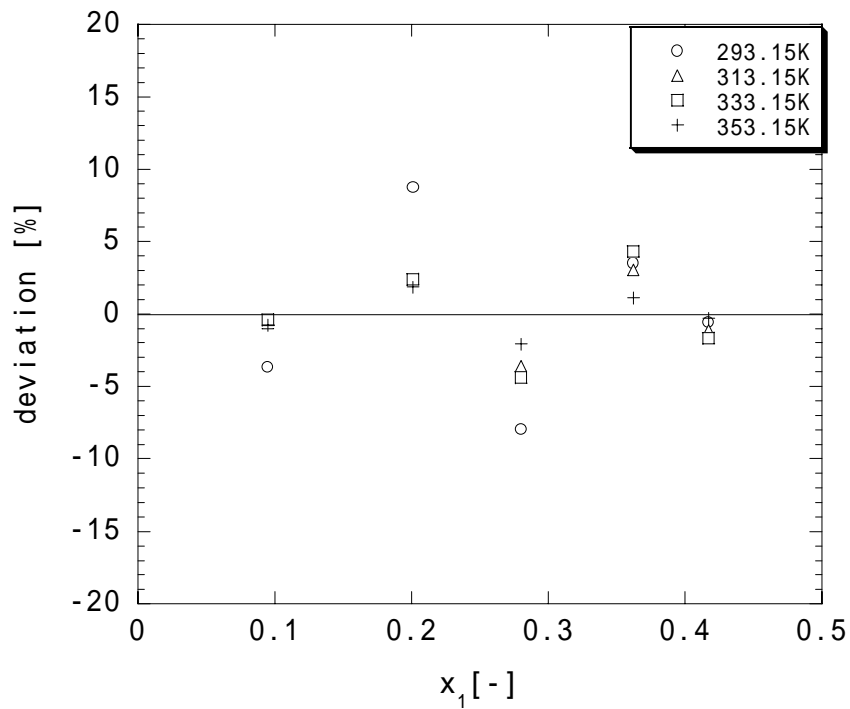


Fig.6 Deviation of kinematic viscosity of squalane + CO₂ mixtures between the experimental data and those calculated from the McAllister equation (at 10MPa).

Table 4 Parameters of the McAllister equation

T[K]	P[MPa]	$\ln v_{1112}$	$\ln v_{1122}$	$\ln v_{2221}$	AAD* [%]	Max Dev.** [%]
293.15	10	-11.765	-10.975	-10.401	4.9	8.7
	15	-12.036	-10.544	-10.377	4.8	-7.8
	20	-12.421	-10.218	-10.325	5.3	-8.6
313.15	10	-11.579	-11.892	-10.911	2.1	-3.6
	15	-12.500	-11.351	-10.870	2.7	-4.5
	20	-12.769	-11.063	-10.897	3.7	-6.2
333.15	10	-11.468	-12.517	-11.445	2.6	-4.4
	15	-11.608	-12.228	-12.524	1.9	3.3
	20	-12.346	-11.832	-11.423	2.6	-4.4
353.15	10	-11.847	-12.858	-11.960	1.2	-2.1
	15	-11.613	-12.913	-11.812	1.3	2.7
	20	-13.124	-11.995	-11.928	2.0	-3.3

* Average absolute deviation = $(v_{\text{exp}} - v_{\text{calc}}) / v_{\text{calc}} \times 100$

** Max deviation = $(v_{\text{exp}} - v_{\text{calc}}) / v_{\text{calc}} \times 100$

5. CONCLUSION

The viscosities of the squalane + CO₂ mixture were measured with a rolling ball viscometer to an accuracy of $\pm 3.0\%$. The experimental data for each experimental conditions were correlated with the Grunberg-Nissan equation. This equation correlated the experimental data within $\pm 10.0\%$. The adjustable parameter of the Grunberg-Nissan equation can be expressed by linear function of composition at each temperature and pressure. While the four-body McAllister equation correlated the experimental data within $\pm 8.7\%$, the parameters of this equation could not be expressed as a function of temperature and pressure.

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